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拔毒散中的蜕皮激素①

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Phytoecdysones from *Sida szechuensis*

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The genus *Sida* with about 90 species is distributed widely in the temperate zone in the whole world. *Sida szechuensis*, which is a perennial, half – shrub found throughout the highland of southwestern China and abundant in resources, is one of species of Malvaceae. It is used in Chinese traditional medicine for ulcers, furuncle, dysentery and blood stasis through ethnopharmacological exploration. Modern pharmacological experiments show that it can inhibit platelet aggregation (Xiao *et al*, 1997). However, to our knowledge, the study on the chemical constituents of this plant has not been reported as yet. In the course of our search for bioactive natural products, three phytoecdysones, (– ecdysone (1), (– ecdysone (2) and polypodine B (3) were isolated and identified from this herb.

The whole plant of *Sida szecheuensis* was purchased from Kunming Company of Medicine, Yunnan, China, in August, 1998, and identified by Jingsheng Yang. A voucher specimen was deposited in the Herbarium of Kunming Institute of Botany, Academia Sinica.

The air – dried powdered material of the whole plant (1.5 kg) was extracted three times in refluxing with EtOH for 2 hr, the solution of EtOH was decolored with active charcoal and then concentrated a in vacuum to provide a residue. The residue was dissolved in H_2O and extracted with petroleum ether, $CHCl_3$ and n – BuOH successively, the $CHCl_3$ layer was evaporated in vacuum to afford extract (5.5 g), the extract was subjected to Silica gel column chromatography, eluting with $CHCl_3$ by increasing amounts of CH_3COCH_3, and fractions A – F were obtained. Fraction A was submitted to silica gel column chromatography with petroleum ether – CH_3COCH_3 (6∶1) to yield compound (1) (17 mg, 0.11%). Fraction E was separated on silicagel chromatography with CHCl3 – MeOH (10∶1) to obtain compound (2) (10 mg, 0.07%) and compound (3) (14 mg, 0.09%).

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Table 1 ^{1}H NMR spectra data of compound (1), (2) and (3) in $C_5D_5N^*$

Hydrogen	1	2	3
H-2	4.04 (1H, m)	3.86 (1H, m)	3.87 (1H, m)
H-3	4.13 (1H, m)	4.18 (1H, m)	4.30 (1H, m)
H-7	6.20 (1H, d)	6.26 (6H, d)	6.27 (1H, d)
H-9	3.54 (1H, t)	3.59 (1H, t)	3.65 (1H, t)
H-17	3.03 (1H, dd)	3.02 (1H, dd)	2.98 (1H, t)
H-18	0.71 (3H, s)	1.19 (3H, s)	1.20 (3H, s)
H-19	1.06 (3H, s)	1.06 (3H, s)	1.15 (3H, s)
H-21	1.28 (3H, d)	1.59 (3H, s)	1.60 (3H, s)
H-22	4.21 (1H, ddd)	4.23 (1H, dd)	4.20 (1H, dd)
H-26, 27	1.37 (6H, s)	1.36 (6H, s)	1.38 (6H, s)

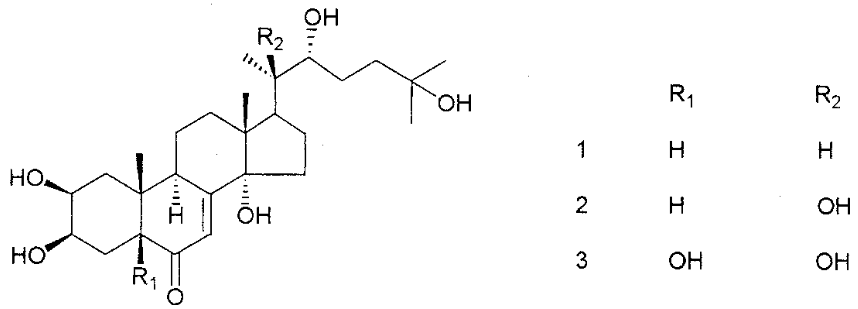
* TMS as the internal standard.

Table 2 ^{13}C NMR spectra data of compound (1), (2) and (3) in $C_5D_5N^*$

Carbon	1	2	3	Carbon	1	2	3
1	38.01t	38.05t	34.84t	15	31.46t	31.79t	31.69t
2	68.09d	68.12d	69.94d	16	25.69t	21.8at	22.15t
3	68.09d	68.12d	68.08d	17	48.36d	50.19d	50.12d
4	32.42t	32.46t	36.14t	18	15.84q	17.90q	17.97q
5	51.40d	51.42d	79.97s	19	24.50q	24.49q	17.24q
6	203.46s	203.37s	201.18s	20	43.02d	76.92s	77.06s
7	121.60d	121.71d	120.03d	21	13.69q	21.71q	21.74q
8	165.60s	166.00s	166.97s	22	74.05d	77.61d	77.76d
9	34.59d	34.52d	39.91d	23	26.70t	27.52t	27.54t
10	38.70s	38.69s	44.90d	24	42.51t	42.64t	42.65t
11	21.14t	21.53t	21.49t	25	69.72s	69.61s	69.94s
12	31.98t	32.07t	32.17t	26	30.04q	29.99q	30.06q
13	47.61s	48.17s	48.23s	27	30.26q	29.99q	30.06q
14	83.89s	84.26s	84.22s				

Compound (1): $C_{27}H_{44}O_6$, M 464, colorless crystals (EtOAc-MeOH), mp 233~235℃; UV λ_{max}^{EtOH}242; IR $\nu_{max}^{KBr}cm^{-1}$: 3414, 2966, 2877, 1710, 1653, 1464, 1448, 1381, 1318, 1282, 1265, 1226, 1208, 1148, 1124, 1055, 997, 949, 936, 910, 879; EIMS 70eV m/z (%): 464 (M^+, 1), 446 (M^+-H_2O, 9.5), 430 (M^+ -2OH, 36), 428 (M^+-2H_2O, 28), 415 (430-Me, 21), 412 (430-H_2O, 21), 410 (M^+-3H_2O, 8), 396 (10), 372 (8.5), 361 (10), 348 (M-$C_6H_{13}O_2$+H, 29), 330 (348-H_2O, 38), 315 (348-H_2O-Me, 33), 300 (315-Me, 38), 285 (300-Me, 13), 277 (30), 263 (15), 250 (36); 161 (29), 147 (38), 126 (side chain-H2O-H, 48), 109 ($C_8H_{17}O_2-2H_2O$, 47), 99 ($C_6H_{13}O_2-H_2O$, 100), 91 (49), 81 ($C_6H_{13}O_2-2H_2O$, 81.5), 69 (68); The above evidences, together with its ^{13}C and ^{1}H NMR, suggested that compound (1) should be assigned as α-ecdysone. The assumption was further confirmed by comparing the spectra data and melting point of compound (1) with those of α-ecdysone reported in the literatures (Nakano *et al*, 1981). Thus, compound (1) was represented as α-ecdysone (2β, 3β, 14α, 22R,

25 – pentahydroxy – 5β – cholest – 7 – en – 6 – one).



Compound (2): $C_{27}H_{44}O_7$, M 480, white crystals (EtOAc – MeOH), mp 237 ~ 240 ℃; UV λ_{max}^{MeOH} 242 nm; IR ν_{max}^{KBr} cm^{-1}: 3422, 2965, 2927, 2854, 1717, 1655, 1448, 1382, 1226, 1148, 1057, 954, 879, 908, 535; EIMS 70 eV m/z (%): 444 (M – 2H2O, 7), 426 (M – $3H_2O$, 35), 411 (426 – Me, 18), 363 (M – $C_6H_13O_2$, 25), 345 (363 – H_2O, 64), 328 (363 – H_2O – OH, 54), 313 (328 – Me, 14), 301 (61), 173 (32), 159 (side chain – H, 21), 143 (side chain – OH, 47), 126 (33), 99 ($C_6H_{13}O_2$ – H_2O, 85), 81 ($C_6H_{13}O_2$ – $2H_2O$, 78), 69 (77); This evidence, combined with its ^{13}C and ^{1}H NMR, indicated that compound (2) was β – ecdysone. Comparison shows its spectra data ware identical with those of β – ecdysone reported in the literatures (Camps *et al*, 1982). This was further supported by direct comparison of the chromatography feature, melting point and mix melting point with a standard sample which we obtained previously (Bathory *et al*, 1982; Hardman *et al*, 1976). Accordingly, compound (2) was determined as β – ecdysone (2β, 3β, 14α, 20R, 22R, 25 – hexahydroxy – 5β – cholest – 7 – en – 6 – one).

Compound (3): $C_{27}H_{44}O_8$, M 496, colorless crystals (EtOAc – MeOH), mp 247 ~ 249 ℃; UV λ_{max}^{MeOH} 243 nm; IR ν_{max}^{KBr} cm^{-1}: 3421, 2967, 2932, 2880, 1712, 1674, 1463, 1382, 1140, 1063, 952, 908, 880, 848, 804, 537, 469; EIMS 70 eV m/z (%): 463 (M – H_2O – Me, 3.5), 444 (5), 442 (M – $3H_2O$, 5), 428 (5.5), 396 (17), 379 (M – $C_6H_{13}O_2$, 50), 361 (379 – H_2O, 50), 343 (379 – $2H_2O$, 11), 345 (14), 325 (379 – $3H_2O$, 15.5), 317 (M – side chain, 10), 301 (10), 279 (18), 250 (14), 189 (20), 161 (side chain, 22), 149 (45), 126 (28), 99 ($C_6H_{13}O_2$ – H2O, 79), 81 ($C_6H_{13}O_2$ – $2H_2O$, 73), 69 (74); These proofs displayed that compound (3) was polypodine B. Its spectra data and melting point were also consistent with those of Polypodine B reported in the literatures (Camps *et al*, 1982; Group, 1981; Hardman *et al*, 1976). Hence compound (3) was determined to be polypodine B (5β, 20R – dihydroxy – α – ecdysone).

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